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THE DETERMINATION OF ARSENIC.

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INTRODUCTION.

The study of the determination of small amounts of arsenic was begun by the writer about three years ago in the examination of the purity of the seven coal-tar colors that are permitted for use in the coloring of foods by the United States Government. Since then the estimation of arsenic in shellac, glucose, calcium-acid phosphate, baking powders, hops, gelatin, and other products has been undertaken and experience gained from an aggregate of several thousand determinations made in the New York laboratory.

The methods here recommended are concerned with the estimation of amounts of arsenic ranging from 1 micromilligram to 10 or more milligrams and include particularly various modifications of the Sanger-Black-Gutzeit determination of arsenic which seem to improve its accuracy and practicability, new methods for the measuring of the arsin from comparatively large amounts of arsenic, and a new method for the quantitative separation and concentration of varying amounts of arsenic from large quantities of organic and inorganic materials, including in particular the separation from antimony and tin.

DETERMINATION OF SMALL AMOUNTS OF ARSENIC BY A MODIFIED GUTZEIT METHOD.

An article by Sanger and Black [1] covering most of the important factors in the estimation of small amounts of arsenic should be con-

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[1] Soc. Chem. Ind., 1907, **26** : 1115.

sulted, as emphasis will be placed upon the essential points of difference between their method and the one here proposed:

APPARATUS.

The form of apparatus used consists of a generating bottle which may be a 1 or 2 ounce wide-mouth bottle, connected with an upright tube 15 cm in length and 1 cm in diameter, which may be divided into two chambers connected by a rubber stopper, the upper portion containing loosely fitted cotton well moistened with 5 per cent lead-acetate solution and the lower containing lead-acetate paper. Besides the bottle and upright tube is a capillary tube 3 mm in internal diameter and 12 cm in length, carrying the mercuric bromid strip connected by a rubber stopper to the lead-acetate tube or tubes. The lead-acetate paper and cotton usually serve to prevent entirely the passage of hydrogen sulphid, but even if hydrogen sulphid strikes the bromid strip the pale yellow color produced is easily distinguishable from the arsenic stain, which is of a deep orange color.

STANDARDS.

Prepare a tenth-normal arsenous oxid solution by dissolving 4.948 grams to the liter in sufficient sodium hydrate and making slightly acid with sulphuric acid. Standards representing 2, 5, 10, 15, 20, 30, 40, 50, and 60 micromilligrams are prepared from this solution freshly diluted to the proper concentration suitable for exact measurement. The arsenous oxid in 1 cc of this solution may be considered as 5 mg with sufficient accuracy. The diluted solution, it is claimed, rapidly deteriorates,

FIG. 1.—Modified Gutzeit apparatus for the determination of small amounts of arsenic.

and hence should be used immediately after the dilution. The generator is four-fifths filled with 1 to 4 sulphuric acid or 1 to 3 hydrochloric acid. Add now 4 or 5 drops of a 40 per cent stannous chlorid solution in strong hydrochloric acid, and, lastly, 8 to 15 grams of stick zinc, the larger quantity for the larger generator, cut into

several pieces. Close the apparatus and allow to run for an hour at room temperature. It is well to cool the generator at the first of the operation to check the sudden evolution of hydrogen and arsin, particularly when hydrochloric acid is used. The preparation of proper standards is sometimes troublesome for that reason, which difficulty is not encountered in most actual determinations because salts or organic substances are usually present, which have a retarding effect.

The standard stains should be of a deep orange color grading sharply into a short yellow stain and the unaltered white of the mercuric bromid paper. Zinc, sulphuric acid, hydrochloric acid, and other reagents commonly used can be purchased practically free from arsenic. Instead of stick zinc, 4 to 8 grams of granulated or moss zinc may be used, but in the use of the latter the evolution may be too rapid and cooling the generator become necessary. The standard paper is made from heavy, close-textured drafting paper, which is cut into strips 2.5 mm by 12 cm. These strips should possess considerable stiffness to allow ready insertion in the capillary tube. They are sensitized by soaking an hour in 5 per cent alcoholic mercuric bromid solution, taken out (excess of solution rapidly squeezed off), separated on glass rods, and allowed to dry. They are preserved conveniently in a Mason jar.

Mercuric bromid has been found far superior to mercuric chlorid for sensitizing, because of the increased permanence of the stains. No development is practiced with the former and the stains will last six months or more with but little fading, while mercuric chlorid paper undeveloped fades in a few days' time. The stains produced on either of these papers are of a dark orange color and the length of stain indicates the amount of arsenic. If the speed of hydrogen evolution is too rapid, the stain will be drawn out in length and at times entirely yellow. If these yellow stains from the mercuric chlorid paper are developed in ammonia, they give a gray black color indistinguishable from the developed orange stain, thereby giving the appearance of more arsenic than is present.

By regulating the acidity, volume of solution, amount of zinc, and the subsequent rapidity of stain production, uniform results can be obtained.

Various observers from time to time have pointed out the retentive effects of copper, platinum, and iron salts on arsenic. Sanger and Black recommended the platinum and zinc couple to assist the production of hydrogen. Chapman and Law [1] have found tin and cadmium in their alloys, and their salts to be nonretentive. Harkins [2] has recommended the use of stannous chlorid in the Marsh

[1] Analyst, 1906, 31: 3.
[2] J. Amer. Soc., 1910, 32: 518.

generator to counteract the retentive effects of iron salts. Since stannous chlorid sensitizes the zinc nicely, producing a steady flow of hydrogen which the zinc and platinum couple does not do, it serves in conjunction with potassium iodid to effect the reduction of arsenates, as will be discussed later, and its plentiful supply in any laboratory recommends it for use in the Gutzeit or Marsh generator.

INTERFERING SUBSTANCES.

The article of Sanger and Black, previously mentioned, discusses in detail the interference of sulphids, phosphorous acids likely to produce phosphin, and antimony compounds. Oxidation by nitric acid or bromin eliminates the formation of any phosphin and any but small amounts of hydrogen sulphid which are held back by the lead-acetate paper and cotton. In evaporations with nitric and sulphuric acid the presence of nitrous acid should be avoided. In order to effect its absence, allow the sulphur trioxid fumes to continue until almost all have disappeared; or, evaporate to fumes of sulphur trioxid, add a few cc of water, some bromin water, and boil for about two minutes. Antimony, if present, must be separated from the arsenic, as it will interfere if present in the generator. The precipitation of the arsenic with magnesium phosphate serves the purpose admirably, and is given in detail later.

## REDUCTION OF ARSENATES AND ARSENITES BY NASCENT HYDROGEN.

Arsenates are reduced with much more difficulty by nascent hydrogen than arsenites. The reduction of any but very small amounts of arsenic is likely to be tedious and incomplete unless the generator is heated or the action prolonged. It is strongly urged that arsenates be reduced to arsenites. In ideal conditions, where the amount of arsenic is small and the evolution of hydrogen is not affected by organic matter or excessive amounts of salts, the preliminary reduction may be unnecessary.

The reduction is accomplished according to Sanger and Black by boiling with sulphur dioxid, but has not been found to be quantitative at least in 3 or 4 mg quantities working under their conditions. Sutton's Volumetric Analysis, tenth edition, page 156, mentions the great difficulty of reduction by sulphur dioxid. Potassium iodid, together with the stannous chlorid, which latter also serves the purpose of activating the zinc, seems to make a rapid and complete reduction under conditions easily attainable. Arsenates are heated in a 1 to 4 sulphuric-acid or 10 per cent hydrochloric-acid solution with 0.75 gram of potassium iodid to 50 cc of solution and 4 drops of 40 per cent stannous chlorid solution near the boiling point for 10 minutes. The stannous chlorid takes up all the iodin liberated (no

free iodin should be present at any time). That the reduction is quantitative can be shown by adding a very dilute solution of stannous chlorid from time to time to take up the liberated iodin. The liberation of iodin soon ceases. At this point if a very small amount of arsenate be added iodin is liberated immediately; or, the solution of arsenous acid may now be titrated, after cooling, neutralizing, etc., with iodin.

THE DETERMINATION OF LARGER AMOUNTS OF ARSENIC.

The preceding method is limited to small amounts of arsenic varying from 1 to 60 or 70 micromilligrams. Where larger amounts are present proportional quantities should be taken. If amounts from 200 micromilligrams to 10 mg or even more can be suitably concentrated for the generator they may be very accurately and rapidly determined by passing the arsin into mercuric chlorid solution. The arsin in its reactions with mercuric chlorid probably forms several different arsenids and that which appears to be free arsenic inside the tube leading into the solution where the arsin is in large excess. No attempt has been made to identify these compounds, but whatever they may be, they are oxidized by the excess of mercuric chlorid slowly in the cold and rapidly on heating, forming arsenous acid and calomel. The effect of light has been observed to be highly accelerating in the decomposition. The iodin absorption before or after this transformation represents the oxidation of arsin to arsenic acid in which 1 As is equivalent to 8 I. The accuracy of iodometric titrations and the large iodin equivalent makes the titration unusually valuable. Again, after the transformation of the precipitate into calomel is complete, the weight of the calomel may be found. One milligram of arsenous oxid (As_2O_3) is equivalent to 14.26 mg of calomel. The equation used for this calculation is:

$$2 \ AsH_3 + 12 \ HgCl_2 + 3 \ H_2O = 12 \ HgCl + As_2O_3 + 12 \ HCl$$
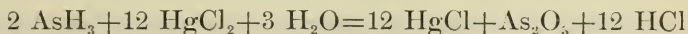
Therefore 1 As_2O_3 is equivalent to 12 HgCl. In the titration, 1 mg of arsenous oxid is equivalent to 8.08 cc of hundredth-normal iodin. The arsenous oxid in the filtrate from the calomel may be titrated with hundredth-normal iodin after the addition of sodium bicarbonate, but here the titration is one-fourth the titration from arsin to arsenic acid.

APPARATUS.

For the generator, a 2-ounce wide-mouth bottle has been found quite practicable. It is connected with a right-angle tube having a bulb blown near the bottle to prevent trapping. The right-angle tube is connected with a horizontal tube 15 cm by 1 cm containing cotton moistened with 5 per cent lead-acetate solution, which is in

turn connected with a right-angle tube ending in a capillary point. This latter tube passes to the bottom of a solution containing 5 cc of a 5 per cent mercuric-chlorid solution diluted to a volume of about 60 cc contained in a vessel of such proportion that the height of the liquid is about 5 cm. If the amount of arsenous oxid is more than 5 mg, 1 cc of mercuric-chlorid solution for each additional milligram should be present. A slender, wide-mouth, lipped Erlenmeyer flask of 100 cc capacity is suitable for both titrating and weighing. It would be advisable for the analyst to arrange to stopper the flask
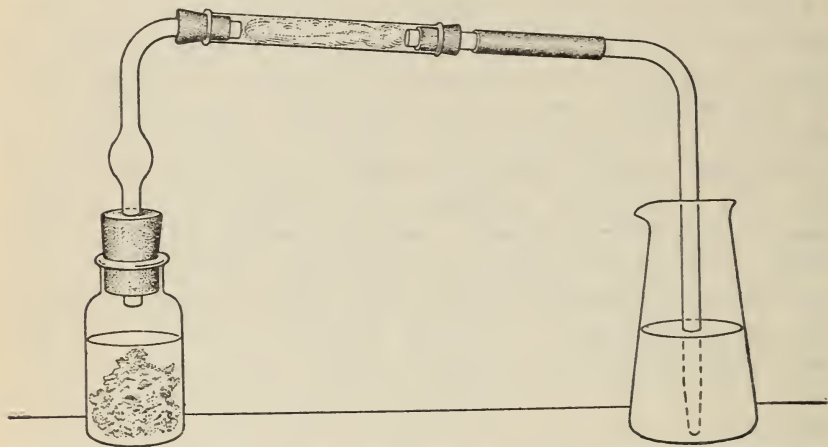

FIG. 2.—Modified Gutzeit apparatus for the determination of larger amounts of arsenic.

and test the exit gas with a mercuric-bromid or chlorid strip, as in the modified Gutzeit method, and the efficiency of the absorption being assured, the testing may be omitted.

TITRATION AND WEIGHING OF THE MERCURIC-CHLORID PRECIPITATE.

If it is desired to titrate the conglomerate precipitate, sufficient potassium iodid (1 cc of 15 per cent potassium-iodid solution for each cubic centimeter of mercuric-chlorid solution) is added to form the soluble double potassium-mercuric iodid and then an excess of standard iodin solution representing about 25 per cent excess is added to dissolve the precipitate, and a clear solution is obtained. A policeman is occasionally necessary to break up the deposit on the bottom of the flask; tenth-normal and fiftieth-normal iodin solutions are convenient strengths. The excess is finally determined by hundredth-normal thiosulphate with starch as indicator. The iodin solution is standardized on tenth-normal arsenous oxid solution or compared with pure iodin. The hundredth-normal thiosulphate is prepared by dilution of standard tenth-normal thiosulphate when needed. On account of the occasional difficulty encountered in dissolving the pre-

cipitate as first formed with the iodin, it is thought preferable to convert the precipitate into pure calomel which may be then titrated or weighed. In order to transform the precipitate entirely into calomel the solution is gently boiled for about 30 minutes, when the whole should be completely white. If the precipitate is to be weighed it is filtered on an ignited gooch, washed with alcohol, dried from 100° to 105° C. for 30 minutes, weighed, and finally the calomel is volatilized by heating in a muffle at low redness for 10 minutes and again weighed. The arsenous oxid in the filtrate may be titrated after filtering off the calomel and adding a little sodium bicarbonate. The titration is one-fourth that obtained in passing from arsin to arsenic acid. It seems probable that the arsenous acid could be recovered in some simple way, so that it could be redetermined or suitable qualitative tests applied, but no experiments have been made as yet in this direction.

The following tables give the results of arsenic determinations:

TABLE 1.—*Determination of arsenic by titration.*

Experi- ment No.	Arsenous oxid.		Theory.	Hydro- chloric acid.	Remarks.
	Taken.	Found.			
	Mg.	*Mg.*	*Per cent.*	*cc.*	
1	4.00	3.85	96.2	5	Unoxidized.
2	4.95	5.00	101.0	15	Do.
3	1.98	2.02	102.0	15	Do.
4	9.90	9.92	100.2	15	Do.
5	4.00	1.09	27.0	5	Oxidized by bromin.
6	4.00	2.20	55.0	15	Do.
7	4.00	4.00	100.0	15	Oxidized by bromin and reduced by potassium iodid.
8	.20	.20	100.0	15	Do.
9	2.475	2.44	98.6	15	Do.
10	2.475	2.51	101.4	15	Do.
11	2.475	2.51	101.4	15	Do.
12	4.95	4.80	97.0	15	Do.
13	4.95	4.76	96.2	15	Do.

TABLE 2.—*Determination of arsenic by weighing the calomel.*

Experi- ment No.	Arsenous oxid taken.	Calomel.	Arsenous oxid found.	Theory.	Remarks.
	Mg.	*Mg.*	*Mg.*	*Per cent.*	
1	4.95	71.2	4.99	100.8	Unoxidized.
2	2.47	35.9	2.52	102.0	Do.
3	4.95	70.9	4.97	100.4	Do.
4	9.90	140.2	9.83	99.3	Do.
5	9.90	142.1	9.96	100.6	Oxidized and reduced.
6	2.47	35.1	2.46	99.5	Do.
7	.99	14.0	.98	99.0	Do.
8	.99	14.1	.98	99.0	Unoxidized.
9	4.95	69.9	4.89	98.9	Oxidized and reduced.
10	.49	6.7	.47	98.0	Unoxidized.
11	4.00	59.5	4.17	104.2	Do.
12	4.00	58.9	4.13	103.0	Do.
13	6.00	86.4	6.06	101.0	Do.
14	8.00	112.4	7.88	98.5	Do.
15	10.00	137.3	9.63	96.3	Do.
16	10.00	147.4	10.33	103.3	Do.

TABLE 3.—*Determination of arsenic by titration of the filtrate from the calomel.*

Experi-ment No.	Arsenous oxid taken.	Titration hundredth-normal iodin.	Arsenous oxid found.
	Mg.	*cc.*	*Mg.*
1	4.95	10.5	5.2
2	2.47	5.3	2.6
3	4.95	10.4	5.2
4	9.90	21.0	10.5
5	9.90	20.8	10.4
6	2.47	5.2	2.6
7	.99	2.2	1.1
8	.99	2.2	1.1
9	4.95	10.2	5.1

In following the course of arsenic evolution in the above methods many experiments were run in which the apparatus was disconnected, the generator put in direct connection with the tubes and a strip of bromid paper as used in the modified Gutzeit method, and the residual arsenic determined. These results could not well be tabulated, but they indicated the superiority of using moss zinc (about 6 grams) and cooling the generator to about 10° C. at the beginning of the determination, to insure the complete evolution of the arsin. In about 10 minutes the generator can be run at room temperature. At the end of an hour there may be 1 or 2 per cent of the arsenic left. The generator may be opened, 5 to 10 cc of fresh concentrated hydrochloric acid introduced, and the action continued for another hour. Heating is usually unnecessary.

The advantage of reduction of the arsenic acid is shown by comparison of many of the results with the two results included in which the arsenate was not reduced. That heating and the fresh addition of acid would finally convert all the arsenic acid into arsin is doubtless true, but the conversion is several times slower than from arsenous acid to arsin. It has been found in the determination of arsenic in calcium acid phosphate, gelatin, and other substances, that even amounts like 50 micromilligrams come off very slowly unless the arsenic acid is reduced. The last six results in Table 2 were obtained by E. C. Merrill and represent his first trials of that method.

PREPARATION AND TREATMENT OF SAMPLE FOR ARSENIC DETERMINATION.

Many products, inorganic and organic, may be directly introduced into the generator after slight treatment. More often the sample must undergo considerable treatment. As stated in the introduction, the writer's experience began in the determination of arsenic in

the so-called "food colors." The limit of arsenic permitted by the United States Government is 1 part of arsenous oxid in 700,000 of color. This delicacy meant the working up of large samples to attain quantitative accuracy by the modified Gutzeit method. The ignition of the dyes with sodium carbonate or magnesium oxid was always accompanied by loss of most of the arsenic and was soon given up as worthless. Distillation with hydrochloric acid, as in the Fischer method, was found impracticable. A method was then elaborated which answered quite satisfactorily and which has been in use on colors and other products for more than 2 years. The method consists in adding a large excess of sodium phosphate with the arsenic in the highest state of oxidation and precipitation with magnesia mixture.

The method as applied to Naphthol Yellow S, Amaranth, Ponceau 3 R, other colors, and other products, is to dissolve the sample (in the case of dyes, 10 grams) in 200 cc of water, adding bromin water until in excess, usually about 10 cc altogether, then 20 cc of 10 per cent sodium phosphate solution and precipitating with about 15 per cent excess magnesia mixture. Ammonia is then added until the final concentration is about 2.5 per cent. The whole is allowed to stand for an hour and filtered. The precipitate is washed several times with 2.5 per cent ammonia and finally dissolved in 1 to 4 sulphuric acid or 10 per cent hydrochloric acid and put in the generator, reducing the arsenic acid with potassium iodid, and continuing as in the modified Gutzeit method.

If there is much organic matter left in the precipitate, as is usually the case with dyes, it may be advisable to evaporate the solution of the precipitate in sulphuric acid, with the addition of about 5 cc of nitric acid, until most of the sulphuric acid has fumed off, or to evaporate until the sulphur trioxid fumes begin, adding water and a few cubic centimeters of bromin water and boil for 2 minutes. This latter treatment destroys nitrous acid and sulphur compounds, which may produce hydrogen sulphid in the generator.

This method of precipitating arsenic has been checked as to its quantitative accuracy many times for small amounts, varying from 1 to 70 micromilligrams. Since the elaboration of the methods given in this paper for determining larger amounts, the precipitation of larger amounts has been tested. It should be remembered that magnesium ammonium arsenate is much more soluble in 2.5 per cent ammonia than magnesium ammonium phosphate. Under the conditions here used, 1 mg of arsenic, if precipitated alone, would remain in the solution.

TABLE 4.—*Precipitation of arsenic with magnesium phosphate.*

Arsenous oxid.		Theory.
Taken.	Found.	
Micromilligrams.	*Micromilligrams.*	*Per cent.*
2	2	100
10	11	110
26	24	92
35	30	86
40	41	102
60	53	88
Milligrams.	*Milligrams.*	
0.2	0.192	96
.8	.796	99.5
1.00	1.017	101.7
1.98	1.92	97.0
5.94	5.74	96.6
9.90	9.82	99.0
3.96	3.86	97.4

METHODS APPLICABLE TO ORGANIC AND INORGANIC SUBSTANCES.

GELATIN.

Heat 10 grams of sample with 50 cc of 10 per cent hydrochloric acid on the steam bath for one hour, adding a few cubic centimeters of bromin water after the whole has liquefied. Dilute the limpid solution thus obtained to 100 cc, take aliquots, reduce with potassium iodid and stannous chlorid, and put directly into the generator. Five-gram quantities of gelatin may be treated in the same manner, made alkaline with ammonia, and the arsenic precipitated with magnesium phosphate. This precipitate may be dissolved off with acid and introduced into the generator, reduced, and the arsenic determined as usual.

COPPER.

Dissolve 2 grams of sample in a small amount of nitric acid, precipitate with magnesium phosphate, and continue as usual. Possible retentive effects of copper should be guarded against by a second precipitation, if necessary.

PHOSPHATE BAKING POWDER.

Heat on the steam bath 5 grams of the powder with 50 cc of 10 per cent hydrochloric acid and a few cubic centimeters of bromin for 2 hours or until the starch is hydrolized. Reduce and place directly in the generator and determine the arsenic as usual.

INDIGO CARMIN.

Dissolve 10 grams of sample in 100 cc of hot water; add 15 cc of concentrated nitric acid and boil for 20 minutes. The viscous

solution is then thin and yellow in color. Neutralize with ammonia and precipitate the arsenic with magnesium phosphate.

HOPS.

Hops can be treated similarly to indigo carmin. The complete decomposition with nitric and sulphuric acids is extremely tedious.

SHELLAC.

Decompose with nitric acid until the liquid mass is of a thin consistency and apply the magnesium-phosphate precipitation.

SEPARATION OF ARSENIC FROM ANTIMONY AND TIN.

Arsenic in minute as well as in large amounts can be separated quantitatively from antimony and tin by means of the magnesium phosphate precipitation. In attempting to secure experimental data to establish this point great difficulty was encountered in obtaining potassium antimonyl tartrate, which was to supply the antimony, free from arsenic. One of the samples of potassium antimonyl tartrate tested was a standard brand of analyzed chemicals which purported to be arsenic-free. The test applied was evidently too rigid, for the arsenic amounted to 100 times more than could be well handled by the modified Gutzeit method.

Recrystallization seemed to reduce the arsenic content so slightly that this method of purification was abandoned. If arsenic can be precipitated quantitatively by the magnesium-phosphate precipitation, it should be possible to purify potassium antimonyl tartrate by this means. Two and one-half grams of the potassium antimonyl tartrate and 5 grams of tartaric acid were dissolved in about 130 cc of water contained in a 200 cc graduated flask. Excess of bromin water sufficient to completely oxidize the arsenic and antimony to their pentavalent forms was added, and then the usual magnesium-phosphate precipitation employed. The solution was made up to the mark and aliquots taken for succeeding analyses. The arsenic content, as expected, had been reduced to a very small fraction of the original amount. A single precipitation of arsenic with magnesium phosphate in the presence of large quantities of antimony was found to carry small but interfering amounts of antimony. A second precipitation freed the magnesium-phosphate precipitate entirely from the antimony. Before the first precipitation 10 grams of ammonium chlorid and 5 grams of tartaric acid were added. The first precipitate was dissolved in 50 cc of dilute hydrochloric acid, 2 grams of tartaric acid added, then excess of ammonia to reprecipitate, and the arsenic determined in this precipitate. The following results

were obtained from experiments adding known amounts in the presence of antimony and tin:

Separation of arsenic from antimony and tin.

Arsenous oxid.		Potassium anti-monyl tartrate taken.	Stannous chlorid.
Taken.	Found.		
Micromilligrams.	*Micromilligrams.*	*Grams.*	*Grams.*
25	24	0.25	0.0
50	54	.25	.2
Milligrams.	*Milligrams.*		
4.95	4.91	.25	.0
4.95	4.87	.25	.2

The blank determination on 0.25 gram of the potassium antimonyl tartrate showed 16 micromilligrams of arsenous oxid; this correction was made in obtaining the first two results in the second column. In working with small quantities of antimony amounting to several milligrams a single precipitation is sufficient to insure the absence of interfering amounts of antimony even without the addition of tartaric acid.

From a study of the results obtained, it seems possible to estimate arsenic in amounts of about 1, 2, or 3 parts of arsenous oxid in the presence of 1,000,000 parts of antimony, making use of the magnesium-phosphate precipitation, properly adapted to the conditions imposed, and the modified Gutzeit method.